

PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Polyurethane Polymers.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polyurethane polymers and more particularly to a new process for the preparation of thermoplastic elastomeric polyurethane polymers.

According to the invention there is provided a process for the manufacture of thermoplastic, elastomeric polyurethane polymers which comprises reacting together under slightly acid conditions at a temperature below 100°C., preferably at from 50°C. to 100°C., a substantially linear polyhydroxy compound of molecular weight greater than 800 and preferably between 800 and 5000, and an excess of an organic diisocyanate having an acidity below 0.02% as determined by the method herein described, heating the product so obtained to a temperature of 60 to 150°C. and mixing with a low molecular weight diol supplied to the mixing vessel at a temperature of from 15 to 150°C. with agitation for a period of from 20 seconds to 3 minutes, thereafter discharging the mixture from the mixing vessel, heating it at from 70 to 130°C. until it solidifies and thereafter heating the solidified mixture at a temperature up to 120°C. for a period of from 6 to 40 hours.

By a "low molecular weight diol" is meant a compound having two aliphatically- or alicyclically-bound hydroxyl groups and a molecular weight of at most 250.

As polyhydroxy compounds of molecular weight greater than 800, there may be men-

tioned polyetherthioethers and polyacetals but it is preferred to use a polyester or a polyether. These polymers should preferably be linear but may be slightly branched and should either be liquid or have a melting point not higher than 60°C.

As example of polyethers which can be used there may be mentioned polymers and copolymers of cyclic oxides, for example 1:2-alkylene oxides such as ethylene oxide, epichlorohydrin, 1:2-propylene oxide, 1:2-butylene oxide and 2:3-butylene oxide, oxycyclobutane and substituted oxycyclobutanes and tetrahydrofuran. There may also be mentioned polyethers such as are prepared for example by the polymerisation of an alkylene oxide in the presence of a basic catalyst and water, glycol or a primary monoamine. Mixtures of such polyethers may be used. The preferred polyethers are polypropylene ether and polytetrahydrofuran polymers.

As examples of polyether-thioethers which can be used there may be mentioned the products of the self-condensation of thioglycols such as thiodiglycol or of the condensation of thioglycols with glycols.

The polyesters which can be used may be made by conventional means from aliphatic dicarboxylic acids and dihydric alcohols. Suitable dicarboxylic acids include succinic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic acids and mixtures of these. Small proportions, up to about 20 mole % of phthalic, isophthalic and terephthalic acids can also be used. Suitable dihydric alcohols include ethylene glycol, 1:2-propylene glycol, diethylene glycol, dipropylene glycol, trimethylene glycol, 1:2-, 1:3-, 2:3-, and 1:4-butylene glycols, neopentyl glycol, pentamethylene glycol, and hexamethylene

glycol and mixtures of these. Small proportions of polyols containing more than two hydroxyl groups, for example glycerol, trimethylolpropane or pentaerythritol may also be used. The acid value of polyester used should be less than 6.0 and preferably less than 3. The preferred polyesters have melting points below 60°C. and are derived from glycols having from two to eight carbon atoms and dicarboxylic acids having from four to ten carbon atoms. Particularly suitable are polyesters of molecular weight between 1000 and 2500 derived from such dicarboxylic acids, especially adipic acid, and a glycol or mixture of glycols. Polyesters obtained by polymerisation of cyclic lactones or mixtures of cyclic lactones such as ϵ -caprolactone and its alkyl substituted derivatives are also suitable.

As examples of polyactols which can be used there may be mentioned the reaction products of aldehydes, such as formaldehyde, acetaldehyde and butyraldehyde, with dihydric alcohols such as propylene glycol, butylene glycol, and diethylene glycol. It is preferred that the organic diisocyanate used in the new process should be one having a symmetrical structure, for example, hexamethylene-1,6-diisocyanate, tetramethylene-1,4-diisocyanate, 4,4'-diphenylmethane diisocyanate, 1,4-phenylene diisocyanate and 1,5-naphthylene diisocyanate. Hexamethylene-1,6-diisocyanate and 4,4'-diphenylmethane diisocyanate are particularly suitable.

The low molecular weight diol used in the second step of the new process is preferably one which is capable of reacting with an organic diisocyanate as the sole other reactant to form a crystalline polymer of melting point at least 150°C. Preferred examples of such diols are ethylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,4-bis-(β -hydroxyethoxy)benzene and 1,6-cyclohexanediol.

Small amounts of one or more compounds of the type known to be effective in stabilisation of polymers to light or to oxidative or thermal discolouration or degradation such as alkyl substituted phenolic compounds, may be added. Fillers and pigments can also be added if desired. To minimise interference with the polymer-forming reaction of the diisocyanate, these additives should be dry.

The interaction of the polyhydroxy compound of molecular weight greater than 800 with the isocyanate can be carried out independently of the other steps to give a primary condensation product of excellent stability which can be used as and when required for the remaining stages. For this purpose, the interaction should be carried out under slightly acidic conditions. In addition to providing an intermediate product

of excellent stability, this procedure leads to final condensation products more readily mouldable. The most likely explanation is that such a procedure suppresses side-reactions in which branched chain intermediate condensation products are formed, but the invention is not to be limited by any assumption that this explanation is correct. The amount of acid present should be such as is equivalent to an amount of hydrogen chloride corresponding up to 0.02% by weight of diisocyanate; the lower limit of acidity varies with different polymers, but whether sufficient is present can readily be determined by a trial, and, if necessary, sufficient acid can be added to the mixture to bring the acidity to a desirable level. Either mineral acid or an organic acid can be used, but in the latter case, the acid dissociation constant and potential reactivity with isocyanates should be taken into consideration and if necessary an appropriately larger amount used. Thus, it is usually appropriate to add to the polymeric polyhydroxy-compound about 0.1% by weight of adipic acid prior to its reaction with the diisocyanate. The acidity of the diisocyanate can be measured by adding a measured weight of the diisocyanate to a large excess of *n*-propanol, standing the mixture at ordinary temperatures for about 10 minutes to allow the *n*-propanol and diisocyanate to react together completely, then titrating with a standard solution of potassium hydroxide in alcohol.

The remaining stages are preferably carried out consecutively and in a continuous manner. For example, the primary condensation product and the low molecular weight glycol, at a temperature within the stated ranges can be independently fed to a heated mixing chamber containing a device for mixing the two reactants, and so constructed that the liquid mixture issues onto or into a further heated receptacle such as a moving belt which passes over a platen heated to the required temperature. After a short time the mixture solidifies and can be subjected to the final heating step in the form of a sheet or if desired may be broken into strips or granules before heating. Conventional catalysts for isocyanate reactions, such as organic and inorganic bases and organometallic compounds may be added with the low molecular weight diol if necessary to accelerate the rate of solidification of the reaction mixture.

This final heating stage is preferably carried out in absence of oxygen and moisture, for example, in a closed container, under a blanket of nitrogen or in a vacuum oven.

The proportions of the polyhydroxy compound, isocyanate and diol should be such that the polyhydroxy compound forms from 35 to 80%, preferably 40 to 65% of the total

weight and the isocyanate compound is from 1 to 1.25 times the theoretical amount required to react with all the hydroxyl groups present in the polyhydroxy compound and the low molecular weight diol.

The products obtained by the process of the invention are thermoplastic and are suitable for the production of elastomeric moulded articles by compression moulding, extrusion, calendaring and other commonly-used methods of moulding thermoplastic materials. In order to attain maximum properties it is usually preferred to heat the final moulded article at a temperature up to 120°C. for up to about 24 hours after moulding.

The invention is illustrated but not limited by the following Examples in which parts are by weight.

20 Example 1

1856 Parts of polyethylene adipate having a hydroxyl value of 59.8 mg.KOH/gm. and an acid value of 0.6 mg.KOH/gm., 375 parts of 4,4'-diphenylmethane diisocyanate having an acidity equivalent to 0.002% by weight of hydrogen chloride, and 1.86 parts of adipic acid were heated together at 80°C. for 1 hour and cooled. The resultant product had an isocyanate content of 11.67% by weight.

This product was pumped at a temperature of 105°C. and at a rate of 1500 grams per hour to a mixing unit of about 25 cc. capacity enclosed in an electrical heating element, and with an agitator rotating at 600 r.p.m. By a separate feed-line, 1,4-butanediol at 18° C. was pumped to the mixing chamber at the rate of 167 grams per hour. The heater was adjusted such that the liquid mixture issued at 100° C., the occupancy period in the mixer being just less than one minute. The liquid mixture was allowed to fall on a moving belt made of polytetrafluoroethylene-coated glasscloth which passed over a platen heated at 100° C. After about 1 minute, the mixture solidified and was broken into strips and stoved in a nitrogen atmosphere at 80° C. for 24 hours.

This product was moulded from an injection moulding machine having a barrel temperature of 183° C. and nozzle temperature of 164° C. and then heated in an oven at 105—110° C. for 20 hours, to give material having the following properties:

55	tensile strength	...	537 kg/cm. ²
	elongation at break	...	587%
	permanent set	...	30%
60	modulus at 300% extension	...	212 kg/cm. ²
	hardness	...	92° Shore A.

Example 2

2587 Parts of poly(ethylene adipate) hav-

ing a hydroxyl value of 52.45 mg. KOH/g. and acid value 1.75 mg. KOH/g., 1656 parts of 4,4'-diphenylmethane diisocyanate having an acidity equivalent to 0.002% by weight of hydrogen chloride and 2.58 parts of adipic acid were heated together at 80° C. for 1 hour and cooled. The resultant reaction product had an isocyanate content of 10.57% by weight.

This product was pumped at a temperature of 100° C. and at a rate of 3000 g./hour to a mixing unit of about 25 cc. capacity enclosed in an electrical heating element, and with an agitator rotating at 600 r.p.m. By a separate feed line 1,4-butane diol at 50°C. was pumped to the mixing chamber at the rate of 316 g./hour. The heater was adjusted such that the mixing was conducted at 105° C., the occupancy period in the mixer being about 30 seconds. The liquid mixture was allowed to fall on a moving belt made of polytetrafluoroethylene coated glasscloth which passed over a platen heated at 100° C. After about 1 minute the mixture solidified and after a further 4—5 minutes was broken into strips and stoved in a nitrogen atmosphere at 110° C. for 24 hours.

This product was moulded from an injection moulding machine having a barrel temperature increasing from 170° C. at the rear to 190° C. at the nozzle and then heated in an oven at 105—110° C. for 20 hours to give material having the following properties:

tensile strength	...	600 kg/cm. ²	
elongation at break	...	500%	100
permanent set	...	30%	
modulus at 300% extension	...	222 kg/cm. ²	
hardness	...	50° Shore D	

Example 3

2070 Parts of poly(ethylene adipate) having a hydroxyl value of 52.45 mg.KOH/g. and acid value of 1.75 mg.KOH/g., 1575 parts of 4,4'-diphenylmethane diisocyanate having an acidity equivalent to 0.002% by weight of hydrogen chloride and 2.07 parts of adipic acid were heated together at 80° C. for 1 hour and cooled. The resultant reaction product had an isocyanate content of 12.18% by weight.

This product was pumped at a temperature of 75° C. and at a rate of 3000 g./hour to a mixing unit of about 25 cc. capacity enclosed in an electrical heating element, and with an agitator rotating at 600 r.p.m. By a separate feed line 1,4-butanediol at 50° C. was pumped to the mixing chamber at the rate of 369 g./hour. The heater was adjusted such that the mixing was conducted at 75° C., the occupancy period in the mixer being about 30 seconds. The

liquid mixture was allowed to fall on a moving belt made of polytetrafluoroethylene coated glasscloth which passed over a platen heated at 100° C. After about 1 minute the mixture solidified and after a further 4—5 minutes was broken into strips and stoved in a nitrogen atmosphere at 110° C. for 24 hours.

This product was moulded from an injection moulding machine having a barrel temperature increasing from 170° C. at the rear to 190° C. at the nozzle and heated in an oven at 105—110° C. for 20 hours to give material having the following properties:

tensile strength	... 615 kg/cm. ²
elongation at break	... 512%
permanent set	... 50%
modulus at 300%	
extension	... 285 kg/cm. ²
hardness	... 55° Shore D

Example 4

2575 Parts of poly(ethylene adipate) having a hydroxyl value of 52.87 mg.KOH/g. and acid value of 1.6 mg.KOH/g., 1625 parts of 4,4'-diphenylmethane diisocyanate having an acidity equivalent to 0.002% by weight of hydrogen chloride and 2.57 parts of adipic acid were heated together at 80° C. for 1 hour and cooled. The resultant reaction product had an isocyanate content of 10.42% by weight.

This product was pumped at a temperature of 116° C. and at a rate of 1500 g./hour to a mixing unit of about 50 cc. capacity enclosed in an electrical heating element, and with an agitator rotating at 600 r.p.m. By a separate feed line ethylene glycol at 50° C. was pumped to the mixing chamber at the rate of 111 g./hour. The heater was adjusted such that the mixing was conducted at 130° C., the occupancy period in the mixer being about 2 minutes. The liquid mixture was allowed to fall on a moving belt made of polytetrafluoroethylene glasscloth which passed over a platen heated at 100° C. After about 1 minute the mixture solidified and after a further 4—5 minutes was broken into strips and stoved in a nitrogen atmosphere at 110° for 20 hours.

This product was moulded from an injection moulding machine having a barrel temperature increasing from 170° C. at the rear to 190° C. at the nozzle and heated in an oven at 105—110° C. for 20 hours to give material having the following properties:

tensile strength	... 620 kg/cm. ²
elongation at break	... 650%
permanent set	... 80%
modulus at 300%	
extension	... 270 kg/cm. ²
hardness	... 93 BS°

Example 5

1912 Parts of polytetrahydrofuran having a hydroxyl value of 70.09 mg. KOH/g. and acid value 0.086 mg.KOH/g., 1657 parts of 4,4'-diphenylmethane diisocyanate having an acidity equivalent to 0.002% by weight of hydrogen chloride and 1.91 parts of adipic acid were heated together at 80° C. for 2 hours and cooled. The resultant reaction product had an isocyanate content of 12.64% by weight.

This product was pumped at a temperature of 100° C. and at a rate of 3000 g./hour to a mixing unit of about 25 cc. capacity enclosed in an electrical heating element, and with an agitator rotating at 600 r.p.m. By a separate feed line, 1,4-butanediol at 50° C. was pumped to the mixing chamber at the rate of 372.7 g./hour. The heater was adjusted such that the mixing was conducted at 100° C., the occupancy period in the mixer being about 30 seconds. The liquid mixture was allowed to fall on a moving belt made of polytetrafluoroethylene coated glasscloth which passed over a platen heated at 100° C. After about 1 minute the mixture solidified and after a further 4—5 minutes was broken into strips and stoved in a nitrogen atmosphere at 110° C. for 24 hours.

This product was moulded from an injection moulding machine having a barrel temperature increasing from 180° C. at the rear to 200° C. at the nozzle and heated in an oven at 105—110° C. for 20 hours to give material having the following properties:

tensile strength	... 415 kg/cm. ²
elongation at break	... 460%
permanent set	... 50%
modulus at 300%	
extension	... 240 kg/cm. ²
hardness	... 56° Shore D

Example 6

2007 Parts of poly(propylene ether) glycol having a hydroxyl value of 55.8 mg. KOH/g., 1325 parts of 4,4'-diphenylmethane diisocyanate having an acidity equivalent to 0.002% by weight of hydrogen chloride and 2.007 parts of adipic acid were heated together at 80° C. for 1 hour and cooled. The resultant reaction product had an isocyanate content of 10.66% by weight.

This product was pumped at a temperature of 150° C. and at a rate of 3000 g./hour to a mixing unit of about 25 cc. capacity enclosed in an electrical heating element, and with an agitator rotating at 600 r.p.m. By a separate feed line 1,4-butanediol at 50° C. was pumped to the mixing chamber at the rate of 318 g./hour. The heater was adjusted such that the mixing was conducted at 150° C., the occupancy period

- in the mixer being about 30 seconds. The liquid mixture was allowed to fall on a moving belt made of polytetrafluoroethylene coated glasscloth which passed over a platen heated at 100°C. After about 1 minute the mixture solidified and after a further 4—5 minutes was broken into strips and stoved in a nitrogen atmosphere at 110°C. for 24 hours.
- The product was a thermoplastic material which was readily shaped by injection moulding and extrusion to give tough elastomeric mouldings.
- Example 7**
- 2694 Parts of poly(hexamethyleneadipate) having a hydroxyl value of 57.5 mg.KOH/g. and acid value 2.00 mg.KOH/g., 1744 parts of 4,4'-diphenylmethane diisocyanate having an acidity equivalent to 0.002% by weight of hydrogen chloride and 2.69 parts of adipic acid were heated together at 80°C. for 1 hour and cooled. The resultant reaction product had an isocyanate content of 10.26% by weight.
- This product was pumped at a temperature of 90°C. and at a rate of 3000 g./hour to a mixing unit of about 25 cc. capacity enclosed in an electrical heating element, and with an agitator rotating at 600 r.p.m. By a separate feed line 1,4-butanediol at 50°C., was pumped to the mixing chamber at the rate of 307 g./hour. The heater was adjusted such that the mixing was conducted at 102°C., the occupancy period in the mixer being about 30 seconds. The liquid mixture was allowed to fall on a moving belt made of polytetrafluoroethylene coated glasscloth which passed over a platen heated at 100°C. After about 1 minute the mixture solidified and after a further 4—5 minutes was broken into strips and stoved in a nitrogen atmosphere at 110°C. for 24 hours.
- This product was moulded from an injection moulding machine having a barrel temperature increasing from 170°C. at the rear end to 190°C. at the nozzle and heated in an oven at 105—110°C. for 20 hours to give material having the following properties:
- | | | | |
|---------------------------|-----|-------------------------|----|
| tensile strength | ... | 562 kg/cm. ² | |
| elongation at break | ... | 725% | |
| permanent set | ... | 80% | 95 |
| modulus at 300% extension | ... | 175 kg/cm. ² | |
| hardness | ... | 51 Shore D | |
- Example 9**
- 2640 Parts of poly(ethylene/neopentylene adipate) (70/30 molar) having a hydroxyl value of 62.1 mg.KOH/g. and acid value 1.5 mg.KOH/g., 1235 parts of hexamethylene diisocyanate having an acidity content equivalent to less than 0.002% by weight of hydrogen chloride and 2.64 parts of adipic acid were heated at 100°C. for 2 hours and cooled. The resultant reaction product had an isocyanate content of 12.36% by weight.
- This product was pumped at a temperature of 85°C. and at a rate of 3000 g./hour to a mixing unit of about 25 cc. capacity enclosed in an electrical heating element, and with an agitator rotating at 600 r.p.m. By a separate feed line a mixture of 1500 parts of 1,4-butanediol, 4.0 parts of dibutyltin dilaurate and 1.38 parts of benzoyl chloride at 50°C. was pumped to the mixing chamber at the rate of 407.4 g./hr. The heater was adjusted such that the mixing was conducted at 90°C., the occupancy period in the mixer being about 30 seconds. The liquid mixture was allowed to fall on a moving belt made of polytetrafluoroethylene-coated glass cloth which passed

over a platen heated at 100° C. After about 1 minute the mixture solidified and after a further 4—5 minutes was broken into strips and stoved in a nitrogen atmosphere at

5 80°C. for 36 hours.

This product was moulded from an injection moulding machine having a barrel temperature increasing from 140°C. at the rear to 160°C. at the nozzle and heated in
10 an oven at 105—110°C. for 20 hours to give material having the following properties:

	tensile strength	...	155 kg/cm. ²
	elongation at break	...	370%
15	permanent set	...	120%
	modulus at 300%		
	extension	...	132 kg/cm.
	hardness	...	43 Shore D.

WHAT WE CLAIM IS:—

20 1. A process for the manufacture of thermoplastic, elastomeric polyurethane polymers which comprises reacting together under slightly acid conditions at a temperature below 100°C., preferably at from 50°C.
25 to 100°C., a substantially linear polyhydroxy compound of molecular weight greater than 800 and preferably between 800 and 5000, and an excess of an organic diisocyanate having an acidity below 0.02%
30 as determined by the method herein described, heating the product so obtained to a temperature of 60 to 150°C. and mixing with a low molecular weight diol supplied to the mixing vessel at a temperature of
35 from 15 to 150°C. with agitation for a period of from 20 seconds to 3 minutes, thereafter discharging the mixture from the mixing vessel, heating it at from 70 to 130°C. until it solidifies, and thereafter
40 heating the solidified mixture at a temperature up to 120°C. for a period of from 6 to 40 hours.

2. A process as claimed in claim 1
45 wherein there is used a polyester or a polyether as polyhydroxy compound.

3. A process as claimed in claim 1 or claim 2 wherein there is used a polyhydroxy compound of melting point lower than 60°C.

4. A process as claimed in any of claims 1 to 3 wherein there is used a polyester having an acid value less than 3 as polyhydroxy compound.

5. A process as claimed in any of claims 1 to 4 wherein there is used a polyester of molecular weight between 1000 and 2500 derived from a dicarboxylic acid having from four to ten carbon atoms and a glycol or mixture of glycols having from two to eight carbon atoms.

6. A process as claimed in any of claims 1 to 3 wherein there is used a polypropylene ether polymer or a polytetrahydrofuran polymer as polyhydroxy compound.

7. A process as claimed in any of claims 1 to 6 wherein the organic diisocyanate used is one having a symmetrical structure.

8. A process as claimed in claim 7 wherein the organic diisocyanate used is hexamethylene-1,6-diisocyanate or 4,4'-diphenylmethane diisocyanate.

9. A process as claimed in any of claims 1 to 8 wherein the low molecular weight diol used is one which is capable of reacting with an organic diisocyanate as the sole other reactant to form a crystalline polymer of melting point at least 150°C.

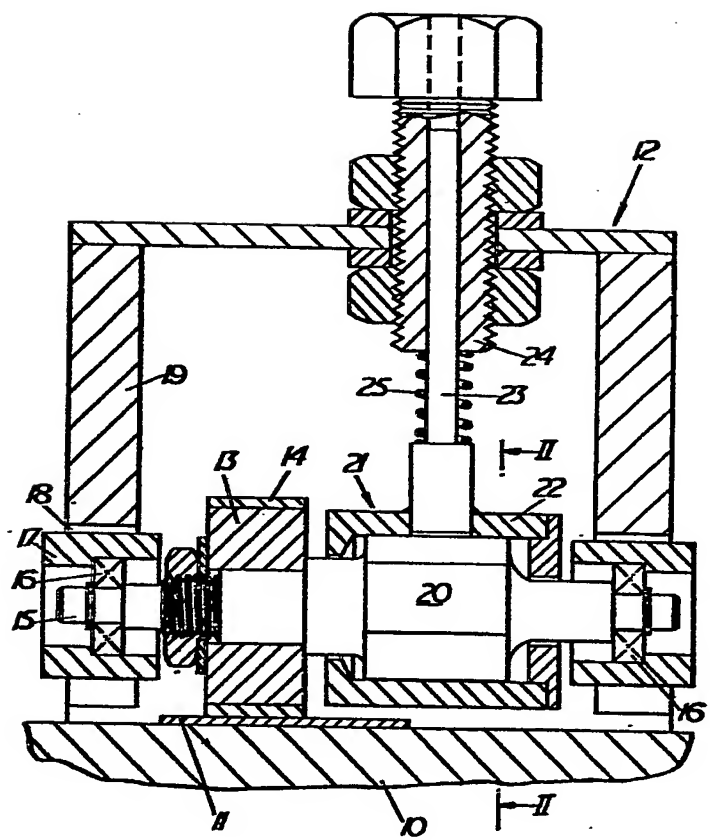
10. A process as claimed in any of claims 1 to 9 wherein the amount of polyhydroxy compound used forms from 40 to 65% of the total weight of reactants.

11. A process for the manufacture of a thermoplastic elastomeric polyurethane polymer substantially as hereinbefore described in Example 1.

12. A process for the manufacture of a thermoplastic, elastomeric polyurethane polymer substantially as hereinbefore described in any one of Examples 2 to 9.

WALTER SCOTT,
Agent for the Applicants.

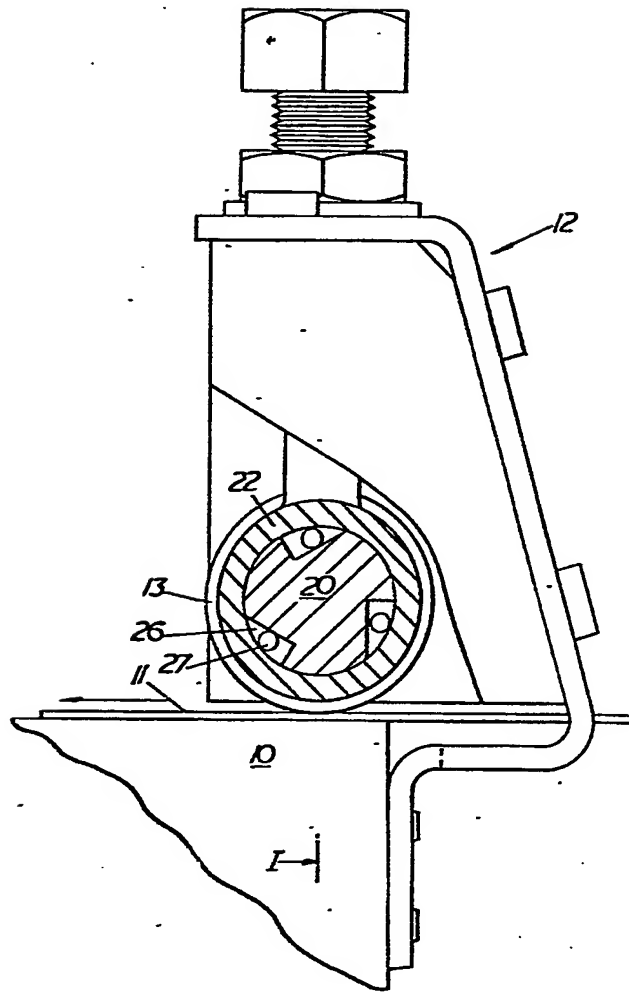
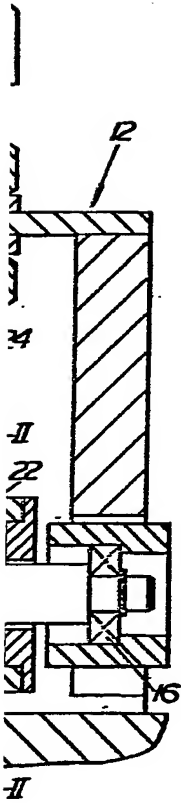
FIG. 1



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FIG 2



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